Semi-Annual Status Report

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by
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The major research areas in this program are concerned with the fundamental radiochemical acts involved in the crosslinking of polymers by means of high energy radiation and the dependence of the crosslinking efficiency and network properties on the state of the system at the time crosslinks are introduced. A major portion of the experimental investigations has been carried out with molecular weight fractions of polyethylene irradiated as a function of temperature and crystallized under controlled conditions from the bulk and from dilute solution. It was shown previously that the temperature must be treated as an independent variable as must the detailed crystallite morphology, particularly the relative amount of crystalline material present and the crystallite size. These general conclusions have necessitated some detailed studies of morphology.

Since the last report a manuscript entitled, "Effect of Morphology and Degree of Crystallinity on the Infra-red Absorption Spectra of Linear Polyethylene" by T. Okada and L. Mandelkern has appeared in the Journal of Polymer Science, A-2, 5, 239 (1967). This paper describes work supported by this grant and gives a detailed correlation with the density and the determination of the degree of crystallinity of linear polyethylene by infra-red methods both at room temperature and at elevated temperatures up to the melting point. Furthermore, by comparing certain regions of the spectra with that of the melt of n-hydrocarbons, it was demonstrated that the structure of the non-crystalline regions is the same as that of the pure melt. It has also been shown that

crystals formed from dilute solution are not completely crystalline but contain 15-20% of the chain units in an amorphous overlayer. The structure of these units is also shown to be the same as that of the melt. The morphological studies of the crystalline polyethylene are being continued with major emphasis on the characterization by means of density measurements and broad line NMR. Of particular interest is the absolute density of crystals formed from dilute solution. This involves assessing the different methods that have been used, the effect of drying the crystals and the dependence of the density on the crystallite size. These measurements together with the previous infra-red results should yield more detailed information in regard to the molecular nature of the interfacial region in such crystals and help in the preparation and understanding of networks formed from them.

A paper entitled, "The Radiation Crosslinking of Hydrogenated Polyethylene" by T. Okada, L. Mandelkern and R. Glick is currently in press in the Journal of the American Chemical Society. By hydrogenating the one vinyl end-group present per molecule we have been able to demonstrate the basis for the previously reported enhanced crosslinking efficiency in the crystalline state. For a hydrogenated sample there is no difference in crosslinking efficiency. However, for the same molecular weight fraction, which is unhydrogenated, the same results as previous are obtained. Thus the enhanced crosslinking efficiency observed in the usual polyethylene sample represents a real effect and is not

a consequence of any experimental artifacts or of chain scission. A unique crosslinking reaction involving the vinyl end-group in the crystalline polymer is indicated which does not necessarily require the production of hydrogen. The crosslinking enhancement is thus a unique and specific chemical effect and would not be generally expected to be observed during the irradiation of other crystalline polymers. These results have also applied to the analysis of the sol-gel partitioning with irradiation dose.

We are presently engaged in analyzing and systematizing the large amount of data that has been obtained with respect to hydrogen evolution, vinyl disappearance, and the formation of trans unsaturation, as a function of molecular weight, level of crystallinity and irradiation dose. Hydrogen evolution and vinyl disappearance are dependent on molecular weight indicating a strong influence of the end-group. It is planned that a manuscript quantitatively describing these results and the possible crosslinking mechanisms will be prepared shortly.

Several new areas of research have been initiated since the last reporting period. It is a matter of interest to study the properties of networks formed from biaxially oriented chains and in particular their dimensional properties. A small scale laboratory apparatus has been developed to allow for the appropriate deformation in the melt and the maintenance of this deformation during crystallization. It is presently being tested utilizing a very high molecular weight sample of linear polyethylene. It is also of interest to study the properties of systems crosslinked in a highly ordered state. Various kinds of preparations are being used in this endeavor. Very high levels of crystallinity can be obtained by crystallizing low molecular weights ($M \leq 20,000$) in the bulk. Such

samples are presently being irradiated. The first results in the pre-gelation indicate a small but significant increase in the melting temperature with irradiation. This could be attributed to either an increase in molecular weight or an entropic effect resulting from the crosslinking of highly ordered chains. These two factors can be sorted out by appropriate experiment, particularly by measurements of the enthalpy of fusion. These latter type of experiments are presently underway.

The preparation of a highly ordered crystalline system comprised of high molecular weight chains cannot be developed by crystallization from the pure melt. It has previously been demonstrated that the level of crystallinity monotonically decreases as the molecular weight decreases. To alleviate this problem conventional type crystals formed from dilute solution are being crosslinked. Although the level of crystallinity is about 85% for such systems even for very high molecular weights, only small size crystallites are developed. Consequently, we are also investigating the properties of crystals formed in dilute solution under the influence of a hydrodynamic shear field. The high orientation that can be achieved by such a method of crystallization has already been established and we are currently investigating the thermodynamic properties and melting behavior of such specimens. Preliminary results utilizing the calorimeter give indications of a melting temperature in excess of 141^{o}C. Confirmation of this observation is being sought in precision dilatometric measurements that are being made presently.